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GEORGETOWN UNIV WASHINGTON D C DEPT OF CHEMISTRY
DOUBLE LAYER STRUCTURE AND ELECTRODE KINETICS.(U)
SEP 80 R DE LEVIE

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The modular "systems" formalism for the description of the admittance of electrode kinetics was applied to membranes, especially to the cases in which membrane-soluble ions cross the membrane, or where ion transport is facilitated by cation carriers, or proton transport by weak acids. The expressions include the effects of the ionic displacement current, which was studied separately in greater detail. Two manuscripts surveyed double layer effects on membranes and at electrodes, while an extensive review discussed the mathematical modeling of ion transport through membranes. Some problems were			

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FINAL SCIENTIFIC REPORT

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"Double layer structure
and electrode kinetics"

The above research program encompassed theory, development of new instrumental methods as well as experimentation. Its accomplishments will be discussed in this order. Numbers in parentheses will refer to the attached list of publications.

The modular "systems" formalism for the description of the admittance of electrode kinetics was applied to membranes, especially to the cases in which membrane-soluble ions cross the membrane (7), or where ion transport is facilitated by cation carriers, or proton transport by weak acids (13). The expressions include the effects of the ionic displacement current, which was studied separately in greater detail (4). Two manuscripts surveyed double layer effects on membranes and at electrodes (1,14), while an extensive review discussed the mathematical modeling of ion transport through membranes (3). We also treated some problems which occur in the application of admittance measurements to a fixed or rotating disk electrode (8).

A new method to analyze electrocapillary data was developed, based on Fourier transformation (2). This efficient method has since been applied successfully in our work on sucrose adsorption, see below. The sampling problem of measurements on a dropping mercury electrode was addressed (12). It was found that the usual errors involved in sampling on the growing mercury surface can be reduced more than an order of magnitude, from over one percent to less than one per mille, by either using averaging over the sampling interval or, for "instantaneous" measurements, by taking into account the transfer function of the specific detector used.

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A novel method was devised and tested to obtain admittance data on time-varying objects such as a dropping mercury electrode. (11). The technique is the digital analog of synchronous detection, with the additional advantages of high speed (even faster than Fourier transformation) and simultaneous detection at a number of different frequencies. It uses the Hadamard transform algorithm.

Extensive double layer studies were made at the water-membrane and water-mercury interfaces. The effect of the neutral compound phloretin, which can modify membrane permeability more than thousandfold by changing the existing dipole potential, could be interpreted quantitatively (5). The effect was used to determine the nature of the phloretin adsorption isotherm.

A boxcar integration method was developed which allows us to measure short-lived transients with our PDP-11 minicomputer. The method yields a time resolution of 0.1 μ s and has been used effectively to establish that the anomalous behavior of dipicrylaminate is due to ion pairing (15).

Extensive ion probe measurements using perbromate, and a combination of dc, ac and pulse polarography, were made in order to measure possible specific adsorption of both fluoride anions and alkaline earth cations on mercury. The fluoride data tested whether the method is useful up to high ionic strengths, where the more classical methods fail; no internal inconsistencies were observed (9). In the case of the alkaline earth cations, the method appears to yield results which are too high, most likely as the result of a "dynamic discreteness-of-charge effect, whereby the probe ion is attracted to the vicinity of the oppositely charged, specifically adsorbed ion, and hence oversamples its presence (10).

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A. D. BLOSE
Technical Information Officer

During efforts to find additional probe ions we found that tetrathionate, a likely candidate, is specifically adsorbed onto mercury even at very low (10^{-4} to 10^{-5} M) concentrations, and is therefore not useful as a probe (6).

Using our fully computer-controlled maximum bubble pressure instrument, we have studied the adsorption of sucrose on Hg from aqueous NaCl solutions (16). Sucrose was selected because it is adsorbed over the entire range of experimentally accessible potentials, and NaCl because activities of the ternary system sucrose-NaCl-water are available. The data obtained show that the mutual effects of sucrose and chloride adsorption are very small, and can be neglected to a first approximation. These measurements also confirm, at least qualitatively, our earlier probe results on specific adsorption of alkali cations (17).

Cumulative list of publications

1. R. de Levie, Ionic adsorption and the conductance of ultrathin lipid membranes. *J. Electroanal. Chem.* 82 (1977) 361-368.
2. R. de Levie, S. Sarangapani, P. Czekaj and G. Behnke, Numerical differentiation by Fourier transformation as applied to electrochemical interfacial tension data, *Anal. Chem.* 50 (1978) 110-115.
3. R. de Levie, Mathematical modeling of transport of lipid-soluble ions and ion-carrier complexes through lipid bilayer membranes, *Advances in Chemical Physics* (I. Prigogine and S. A. Rice, eds.) 37 (1978) 99-137.
4. S. K. Rangarajan and R. de Levie, On the ionic displacement current in lipid bilayer membranes, *Biophys. J.* 25 (1979) 235-252.
5. R. de Levie, S. K. Rangarajan, P. F. Seelig and O. S. Andersen, On the adsorption of phloretin onto a black lipid membrane, *Biophys. J.* 25 (1979) 295-300.
6. T. Ohsaka and R. de Levie, Tetrathionate adsorption onto mercury, *J. Electroanal. Chem.* 99 (1979) 255-258.
7. S. K. Rangarajan, P. F. Seelig and R. de Levie, On the admittance of lipid bilayer membranes I: membrane-permeable ions, *J. Electroanal. Chem.* 100 (1979) 33-62.

8. S. Sarangapani and R. de Levie, On some problems of diffusion towards a circular disk, J. Electroanal. Chem. 102 (1979) 165-174.
9. R. de Levie and T. Ohsaka, The use of kinetic probes in concentrated electrolytes: the reduction of perbromate in KF, in Proceedings of the 3rd Symposium on Electrode Kinetics (S. Bruckenstein, J. D. E. McIntyre, B. Miller and E. Yeager, eds.), (1980) 422-432.
10. T. Ohsaka and R. de Levie, Adsorption of alkaline earth cations on mercury as studied with the perbromate kinetic probe, Bull. Chem. Soc. Japan 53 (1980) 344-346.
11. P. F. Seelig and R. de Levie, Double layer capacitance measurements with digital synchronous detection at a dropping mercury electrode, Anal. Chem. 52 (1980) 1506-1511.
12. R. de Levie, Sampling error in Fourier and Hadamard transform capacitance measurements, Anal. Chem. 52 (1980) 1535-1537.
13. R. de Levie and P. F. Seelig, On the admittance of lipid bilayer membranes II: uncouplers and ion carriers, J. Electroanal. Chem., in press.
14. R. de Levie, The structure of charged interfaces, Sensors and Actuators, in press.
15. R. de Levie and R. J. Atwell Jr., Transport of dipicrylamine across lipid bilayer membranes: evidence for ion pairing, Biophys. J., submitted.
16. M. Krishnan and R. de Levie, On the adsorption of sucrose from aqueous NaCl solutions, in preparation.
17. R. de Levie and M. Krishnan, On subequivalent specific adsorption of ions, in preparation.

Respectfully submitted,



Robert de Levie

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